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ORIGINAL ARTICLE

Oxidation of thioacids by quinaldinium fluorochromate

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Abstract The kinetics of oxidation of thioglycolic, thiolactic and thiomalic acids by quinaldinium fluorochromate [QnFC] has been studied in non aqueous medium. The oxidation kinetics was followed spectrophotometrically in the temperature range of 30–60 °C. The reaction shows unit order dependence each with respect to substrate and oxidant. The reaction is catalysed by hydrogen ions. The hydrogen ion dependence takes the form $k_{obs} = a + b\,[H^+]$. The reaction rate decreases with increasing the concentration of Mn^{2+} ions. The reaction does not induce polymerization of acrylonitrile. A plausible mechanism has been proposed for the formation of a thioester and its decomposition which occur in the slow step.

1. Introduction

A good number of Cr(VI) complexes are being used in the oxidation of organic compounds. Quinaldinium fluorochromate has been used as a mild and stable oxidizing agent in synthetic organic chemistry (Degirmenbasi and Ozgun, 2004). The oxidation of thioacids by pyridinium fluorochromate (Kakuli Chowdhury et al.,1991) and 2,2′-bipyridinium chlorochromate (Rathore et al., 1994) were reported. The reaction of thiocarboxylic acids with electron-deficient organic azides, such as sulfonyl azides (Shangguan et al., 2003) was studied. In the peptide field, this ligation reaction has been applied for the synthesis of neoglycopeptides (Zhu et al., 2004), peptide mimetics (Merkx et al., 2005), C-terminal labelling of peptide thioacids (Zhang et al., 2009), and labelling of sulfonyl azide-modified peptides (Rijkers et al., 2010). Mostly thioacids are used in the convergent synthesis of peptides (Crich et al., 2007) and proteins. On treatment with suitable nucleophile provide very facile access to thioacids (Crich and Bowers, 2007; Mapp and Dervan, 2000) viz., thioglycollic, thiolactic and thiomalic acids. The kinetics of oxidation of thioacids by quinaldinium fluorochromate has not been reported. We report herein the kinetics of the oxidation of thioglycolic, thiolactic and thiomalic acids by quinaldinium fluorochromate with dimethyl sulphoxide as solvent. The mechanistic aspects are also discussed.

2. Experimental

2.1. Material and methods

The thioacids (Aldrich) were commercial products and used as such. The solutions of the thioacids were freshly prepared in

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dimethyl sulphoxide and standardized by titrating it against a standard solution of iodine. Quinaldinium fluorochromate was prepared by the reported method [1] and its purity was checked by an iodometric method. The solvents were purified by usual methods (Perrin et al., 1966). *p*-Toluene–sulphonic acid was used as a source of hydrogen ions.

2.2. Stoichiometry

The stoichiometry of the reaction was determined by performing the experiments under nitrogen at 333 K, under the conditions of $[QnFC]_o > [Thioacid]_o$, at varying concentrations of the acid. The disappearance of Cr(VI) was monitored until a constancy in the absorbance values was attained. The $[QnFC]_\infty$ was estimated. A stoichiometric ratio $\Delta[QnFC]/\Delta[Thioacid]$ was obtained. The reaction exhibited as 1:2 stoichiometry.which confirmed the overall equation

$$R\text{–}S\text{–}H + O_2CrFOQnH \rightarrow R\text{–}S\text{–}S\text{–}R + H_2O + CrOFO - QnH \quad (1)$$

2.3. Kinetic measurements

The reaction was performed under pseudo-first order conditions by keeping the thioacids in quinaldinium fluorochromate and dimethyl sulphoxide as a solvent. The reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions and were followed up to ca 80% conversion by monitoring the decrease in the [QnFC] at 376 nm on the spectrophotometer (Elico Scanning mini Spectrophotometer-Model SL177). The pseudo-first order rate constants, k_{obs}, were evaluated from the linear plot ($r = 0.994$–0.999). The rate constants were obtained from the slope of the plot of log absorbance versus time by the linear least square method. The results were reproducible within $\pm 3\%$. The second order rate constants were evaluated from the relation $k_2 = k_{obs}/[reductant]$.

3. Results and discussion

3.1. Kinetic dependence

The reaction was found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of log [QnFC] versus time ($r = 0.998$). The pseudo-first order rate constants were found to be independent of the initial concentration of the quinaldinium fluorochromate. At constant [QnFC], the rate constants increased with an increase in the concentration of substrate. A plot of log k versus log [substrate] gave a straight line with a slope of unity. This was further well demonstrated by the constancy of the second-order rate constant $k_2 = k_1/[substrate]$ (Table 1).

3.2. Effect of acidity

The reaction is catalysed by hydrogen ions (Table 2).The hydrogen ion dependence takes the form of $k_{obs} = a + b[H^+]$. The values of a and b, for TMA, are 7.84×10^{-1} s^{-1} and 10.07×10^{-1} mol^{-1} dm^3 s^{-1}, respectively ($r = 0.999$).

3.3. Effect of solvent

The reaction was carried out at five different percentages of DMSO-DMF mixtures while all other factors are constant. The reaction is facilitated by the medium of low dielectric constant (ε) and it decreases by the addition of DMF [Table 3].The plot of log k versus the inverse of the dielectric constant gave a straight line with a positive slope. This indicates the presence

Table 2 Effect of hydrogen ion concentration on the oxidation of thioacid by quinaldinium fluorochromate.

[TsOH] 10^3 mol dm^{-3}	k_{obs} 10^4 s^{-1}
1.25	7.83
2.50	15.84
3.75	25.11
5.00	33.88
6.25	43.65

[QnFC] = 3.00×10^{-3} mol dm^{-3}, Temperature = 313 K.
[TMA] = 7.50×10^{-3} mol dm^{-3}.

Table 3 Effect of solvent.

DMSO-DMF (%v/v)	ε	k_1 10^4 s^{-1}
100–0	47.2	7.83
95–5	46.8	9.19
90–10	46.3	11.02
85–15	45.9	13.16
80–20	45.4	16.98

[QnFC] = 3.00×10^{-3} mol dm^{-3}.
[TsOH] = 1.25×10^{-3} mol dm^{-3}.
[TMA] = 7.50×10^{-3} mol dm^{-3}.
Temperature = 313 K.

Table 1 Rate constant for the oxidation of thiomalic acids and quinaldinium fluorochromate.

[QnFc] 10^3 mol dm^{-3}	[TMA] 10^3 mol dm^{-3}	k_{obs} 10^4 s^{-1}	10^1 $k_2 = k_1/[s]$ (l mol^{-1} s^{-1})
2.50	7.50	7.82	1.04
3.00	7.50	7.83	1.04
3.50	7.50	7.83	1.04
4.00	7.50	7.81	1.00
4.50	7.50	7.83	1.04
3.00	5.00	5.07	1.01
3.00	7.50	7.83	1.04
3.00	10.00	10.49	1.05
3.00	12.50	13.18	1.05
3.00	15.00	15.87	1.06

Table 4 Effect of varying concentrations of manganese sulphate.

$[MnSO_4]$ mol dm^{-3}	k_1 10^4 s^{-1}
0.00	7.83
0.50	6.61
1.00	6.35
1.50	6.17
2.00	6.03

[QnFC] = 3.00×10^{-3} mol dm^{-3}.
[TsOH] = 1.25×10^{-3} mol dm^{-3}.
[TMA] = 7.50×10^{-3} mol dm^{-3}.
Temperature = 313 K.

of ion–dipole interaction, (Quinlan and Amis, 1955; Amis, 1966) and consonance with the observation that in the presence of acid, the rate determining step involved a protonated Cr(VI) species (Wiberg, 1965).

3.4. Induced polymerization of acrylonitrile

The oxidation of thioacids by quinaldinium fluorochromate, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile (Littler and Waters, 1959). Further, the addition of acrylonitrile did not affect the rate. This indicates that a one electron oxidation giving rise to free radicals is unlikely in the present reaction.

3.5. Effect of manganese sulphate

The reaction rate decreases with increasing the concentration of Mn^{2+} ions, confirming the involvement of the two electron process in this reaction (Banfi et al., 2000) [Table 4].

3.6. Effect of temperature

The rates of oxidation of three thioacids were determined at different temperatures and it was observed that the rate increased with an increase in temperature (Table 5). From the linear plots of log k_1 against the reciprocal of temperature, the activation energy was calculated. The entropy of activation ($\Delta S^{\#}$) and the free energy of activation ($\Delta G^{\#}$) were calculated using Eyring's equation, respectively (Frost and Pearson, 1970; Peterson et al., 1961).

3.7. Mechanism and rate law

The lack of any radical scavenger such as acrylonitrile on the reaction rate and the failure to induce the polymerization of acrylonitrile, points against the operation of a one electron oxidation giving rise to free radicals. The observed solvent effect supports a transition state, which is more polar than the reactant state. Therefore, a mechanism involving transfer of a direct hydride ion from the S–H group to quinaldinium fluorochromate is suggested (Eqs. (2–4) in Scheme 1).

The above mechanism leads to the following rate which is identical to the experimental observations

$$\text{Rate} = k_2[\text{thioacid}][\text{QnFC}] + k_3[\text{thioacid}][\text{QnFC}][H^+] \quad (5)$$

The above mechanism is supported by the observed activation parameters. Bimolecular reactions usually exhibit negative entropy of activation. As the activated complex is formed the reactants lose their freedom to move independently. Further as, the charge separation takes place in the transition state, the charged ends get solvated by solvent molecules. This results in the immobilization of a large number of solvent molecules and in unfavourable entropy. The observed large negative entropy of activation thus supports the above mechanism.

Exner (1964) criticized the validity of such a good linear correlation between ($\Delta H^{\#}$) and ($\Delta S^{\#}$) as these quantities are dependent on each other. When the measurements at two different temperatures have been made the data can be analysed by the following equation.

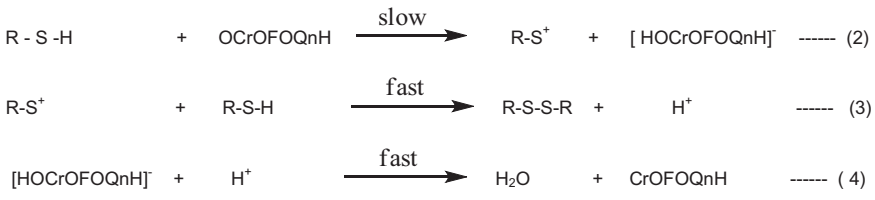
$$\log(k_1)T_1 = a + b\log(k_1)T_2 \quad \text{where } T_2 > T_1$$

The plots of $\log(k_1)_{333K}$ versus $\log(k_1)_{323K}$ gave a good straight line $r = 0.999$ (Fig. 1) and $\log(k_1)_{303K}$ versus $\log(k_1)_{303\text{-}K}$ gave a straight line with $r = 0.998$. Such a good correlation indicates that all the thioacids follow a common mechanism.

Table 5 Activation parameters for the oxidation of thioacids by quinaldinium fluorochromate.

S. no	Thioacids	10^4 k_{obs} (s^{-1})				$\Delta H^{\#}$ (kJmol^{-1})	$-\Delta S^{\#}$ (JK^{-1}mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1}) at 313 K	Ea (kJ mol^{-1}) at 313 K
		303 K	313 K	323 K	333 K				
1	TLA	7.18	11.24	18.08	27.26	34.92	149 .51	94.48	37.52
2	TMA	4.96	7.83	10.93	16.14	29.92	168.94	95.40	32.52
3	TGA	2.48	3.45	4.64	6.71	23.89	194.75	97.53	26.49

[QnFC] = 3.00×10^{-3} mol dm^{-3}.
[TsOH] = 1.25×10^{-3} mol dm^{-3}.
[TA] = 7.50×10^{-3} mol dm^{-3}.



Scheme 1

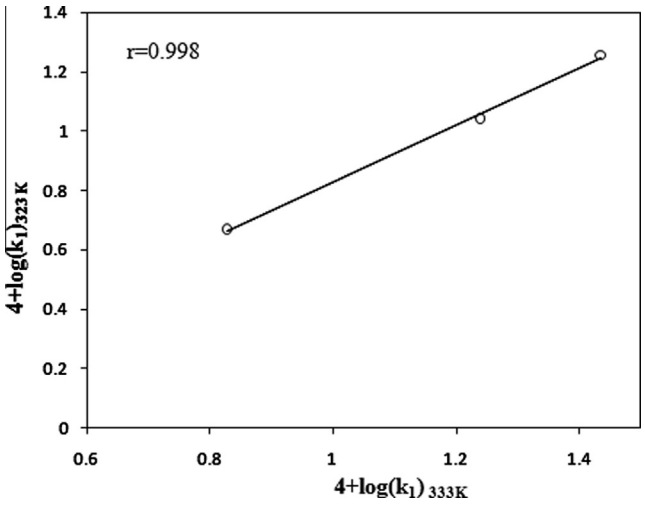


Figure 1 Plot of $\log(k_1)_{323K}$ versus $\log(k_1)_{333K}$.

The formation of a sulphonium cation, in the rate determining step, is supported by the observed major role of cation-solvating power of the solvents.

The proposed mechanism is supported by the relative reactivity also. The observed reactivity is **TLA > TMA > TGA**.

TLA has an electronic donating methyl group, which makes the transfer of a hydride ion easy as compared to that in TGA. In TMA, the presence of a carboxylic acid reduces the electron tendency of the methyl group, reflected at a lower rate. In the presence of hydrogen ions the reactive oxidizing species will be QnFC [H^+]. Although, there is no kinetic evidence for the formation of thioester, its formation in small amounts cannot be ruled out.

4. Conclusions

The oxidation of thioacids by quinaldinium fluorochromate in a non aqueous medium leads to the formation of a complex and finally gives the products. The reaction follows simple order kinetics. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

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